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In organic semiconductors the recombination mechanism is of the Langevin type, controlled by the mobility of the charge carriers. As a result, in organic solar cells the mobility simultaneously controls both the carrier extraction and the losses via carrier recombination. The authors demonstrate that the balance between carrier losses by extraction and by recombination leads to a distinct optimum in the carrier mobility with regard to the efficiency of organic solar cells. For low mobilities recombination losses limit the performance, whereas the efficient extraction at high mobilities leads to a reduction of the open-circuit voltage. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2711534]

The efficiency of solar cells based on bulk heterojunctions (BHJs) of organic semiconductors has significantly increased in the last few years.[1,2] For solar cells based on regioregular poly(3-hexylthiophene) (P3HT) blended with [6,6]-phenyl C_{61}-butyric acid methyl ester (PCBM) efficiencies have been reported ranging from 3.5% for annealed devices,[3] to even more than 4% for slowly dried blends.[4–6] There are a number of processes that contribute to the efficiency of an organic BHJ solar cell.[7] The photogenerated excitons dissociate at the donor-acceptor interface via an ultrafast electron transfer from the donor to the acceptor. In order to dissociate all photogenerated excitons, they should be created within the exciton diffusion length of the interface, putting demands on the morphology. However, the ultrafast electron transfer to the acceptor does not directly result in free carriers, but in a bound electron-hole pair (due to the Coulomb attraction between the carriers). This pair also needs to be dissociated, assisted by temperature and by the internal electric field, before it decays to the ground state.[8] As proposed by the Braun model, this bound pair is metastable, enabling multiple dissociations and being revived by the recombination of free charge carriers.[8] Finally, the free carriers are transported to the electrodes, a process governed by charge carrier mobility.

For organic semiconductors it has been shown that the bimolecular recombination of free carriers, which is a loss process in the solar cells, is of the Langevin type. The recombination rate is given by

$$R = \gamma(np - n_i p_i), \tag{1}$$

where n (p) is the free electron (hole) density, n_i (p_i) is the intrinsic electron (hole) density, and γ is the Langevin recombination constant.[9] The recombination constant for a pristine material is governed by the sum of electron and hole mobilities,[9]

$$\gamma = \frac{q}{\varepsilon}(\mu_n + \mu_p), \tag{2}$$

where q is the elementary charge, ε is the dielectric constant, and $\mu_{n(p)}$ is the electron (hole) mobility. In case of a blend it was proposed that the spatial average of the electron and hole mobilities should be used, in order to compensate for the eventual mobility differences of carriers in the different components of the blend.[8] More recently, it has been shown that the slowest carrier mainly governs the recombination process in the blend; since the fastest carrier cannot cross the interface due to the energy offset between the donor and the acceptor, it must wait for the slowest carrier in order to recombine.[10] As a result, solar cells made of organic semiconductors are special in the sense that the two competing processes, extraction and recombination of charge carriers, are both governed by the mobility of the charge carriers. An increase in carrier mobility would have a positive effect on transport, facilitating carrier extraction, but on the other hand it will increase the bimolecular recombination strength as well. It is therefore not clear what exactly is the role of the mobility with regard to the optimum performance of a solar cell based on organic semiconductors. In this study we investigate the dependence of the solar cell efficiency on charge carrier mobility, using the BHJ device model.[11] We demonstrate that the best device efficiencies are achieved in the mobility range of 10^{-6}–10^{-4} $m^2V^{-1}s^{-1}$. For higher mobilities the efficient extraction of carriers strongly reduces the steady-state charge carrier densities, leading to a reduction of the open-circuit voltage.

In solar cells based on PPV:PCBM blends (1:4 weight ratio) an important loss mechanism is that under short-circuit conditions only 60% of all the bound electron-hole pairs dissociate into free carriers at room temperature.[12] In these blends, the hole mobility, which is one order of magnitude lower than electron mobility,[13] governs the recombination. With annealed P3HT:PCBM solar cells (1:1 weight ratio), higher efficiencies have been obtained, not only due to an increased light absorption because of a higher polymer frac-

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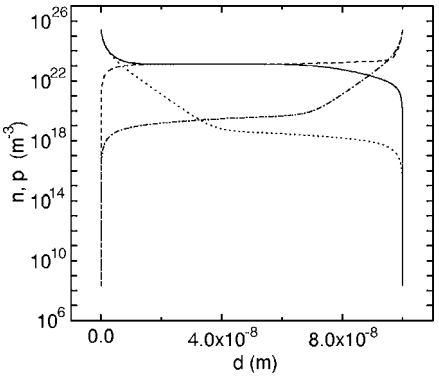

FIG. 1. Carrier densities at short circuit vs the distance from the cathode, for an electron mobility of 1.0×10^{-10} m^2 V^{-1} s^{-1} (hole mobility of 1.0×10^{-11} m^2 V^{-1} s^{-1}): electrons (solid line) and holes (dashed line) and for an electron mobility of 1.0×10^{-5} m^2 V^{-1} s^{-1} (hole mobility of 1.0×10^{-6} m^2 V^{-1} s^{-1}): electrons (dotted line) and holes (dash-dotted line).

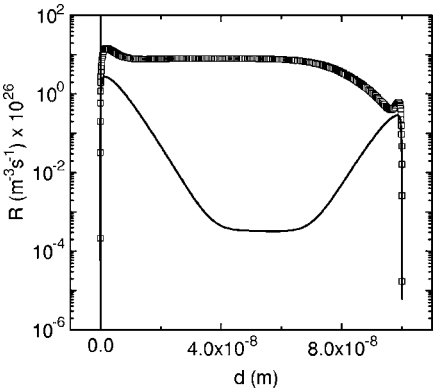

FIG. 2. Recombination rate at short circuit vs the distance from the cathode for an electron mobility $\mu_n=1.0\times10^{-10}$ m^2 V^{-1} s^{-1} ($\mu_p=1.0\times10^{-11}$ m^2 V^{-1} s^{-1}) (squares) and for $\mu_n=1.0\times10^{-5}$ m^2 V^{-1} s^{-1} ($\mu_p=1.0\times10^{-6}$ m^2 V^{-1} s^{-1}) (solid line).

tion in the blend, but in this case also the dissociation process is more efficient.[7] The carrier mobilities for the P3HT:PCBM blend (1:1 weight ratio) are comparable to the PPV:PCBM (1:4 weight ratio) blends,[7] with $\mu_n\sim10^{-7}$ m^2 V^{-1} s^{-1} and $\mu_p\sim10^{-8}$ m^2 V^{-1} s^{-1}. The first question we want to address is how the efficiencies of these devices will be affected when the mobility is lowered. For this comparison all other device parameters are kept the same, including a 10:1 ratio of electron mobility versus hole mobility. A lower mobility of both carriers will lead to a slower extraction of the charge carriers as well as a reduced Langevin recombination, leading to a longer lifetime of the photogenerated carriers. The combination of these two effects strongly affects the steady-state buildup of charge carriers in the solar cell. In Fig. 1 the electron and hole densities in the solar cell are calculated for electron mobilities of 1.0×10^{-10} m^2 V^{-1} s^{-1} (hole mobility of 1.0×10^{-11} m^2 V^{-1} s^{-1}) and 1.0×10^{-5} m^2 V^{-1} s^{-1} (hole mobility of 1.0×10^{-6} m^2 V^{-1} s^{-1}). In this calculation all device parameters have been taken identical as the ones found for annealed P3HT:PCBM devices; an active layer thickness of 100 nm, a maximum generation rate $G_{\max}=6.0\times10^{27}$ m^{-3} s^{-1}, a spatial average of the relative dielectric constant $\varepsilon_r=3.4$, a difference between the ionization potential of the polymer and electron affinity of the acceptor $E_g=1.0$ eV, and the dissociation parameters $a=1.8$ nm and $k_F=1.4\times10^4$ s^{-1}.[7]

As shown in Fig. 1 the steady-state carrier concentrations under 1 sun illumination typically increase by five orders of magnitude in the middle region of the device, when the mobility is lowered by five orders of magnitude. As can be seen from Eqs. (1) and (2) the strong increase of the carrier densities then leads to a strong enhancement of the carrier recombination; since n and p vary each as much as the mobility, the reduction of the Langevin recombination constant γ [Eq. (2)] by a lower mobility is overruled by the product of n and p [Eq. (1)]. In Fig. 2 the amount of bimolecular recombination is calculated at short circuit. For an electron mobility of 1.0×10^{-10} m^2 V^{-1} s^{-1} (hole mobility of 1.0×10^{-11} m^2 V^{-1} s^{-1}), 45% of the carriers recombine at short circuit conditions, as compared to only 0.38%, in case of an electron mobility of 1.0×10^{-5} m^2 V^{-1} s^{-1} (hole mobility of 1.0×10^{-6} m^2 V^{-1} s^{-1}).

It should be noted that for higher recombination a limit is reached when all the carriers recombine. In that case, the steady-state photocurrent is approximately given by[14]

$$J_{\rm ph}=q(G/\gamma)^{1/2}(\mu_n+\mu_p)F_{\rm av}, \tag{3}$$

where q is the elementary charge, G is the generation rate of electron-hole pairs, γ is the recombination strength, $\mu_{n(p)}$ is the electron (hole) mobility, and $F_{\rm av}$ is the average applied electric field. Our simulations show that when 98% of the carriers recombine at short circuit, the calculated photocurrent is identical to the analytical expression given by Eq. (3). Experimentally, such a recombination dominated solar cell is characterized by a dependence of the photocurrent on the light intensity I with a power of 0.5 (assuming $G\sim I$) and a fill factor close to 25%.

The dissociation of a bound-electron hole pair is a field and temperature dependent process, with a probability given by[8]

$$P(E,T)=\frac{k_D(E,T)}{k_D(E,T)+k_F(T)}, \tag{4}$$

where k_D is the dissociation rate constant of the electron-hole pair and k_F is the decay rate to the ground state. The dissociation rate constant k_D is proportional to the Langevin constant γ of charge carriers ($k_D\sim\gamma$),[8] a process which revives the electron-hole pair, and as mentioned above, is governed by the carrier mobility. As a result, the dissociation efficiency is also governed by the charge carrier mobility. In Fig. 3 the dissociation probability at the maximum power point ($M_{\rm pp}$) is shown as a function of electron mobility.

It appears that for mobilities lower than 1.0×10^{-5} m^2 V^{-1} s^{-1} the dissociation probability starts to de-

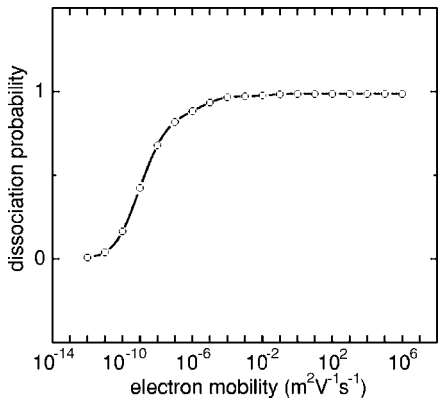

FIG. 3. Dissociation probability at $M_{\rm pp}$ vs electron mobility, corresponding to efficiency values in Fig. 5.

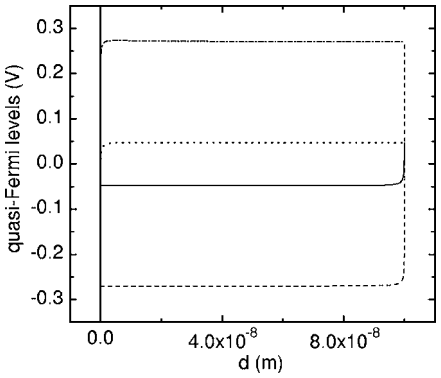

FIG. 4. Quasi-Fermi levels vs the distance from the electron injecting contact for $\mu_n = 1.0 \times 10^{-5}$ m^2 V^{-1} s^{-1} ($\mu_p = 1.0 \times 10^{-6}$ m^2 V^{-1} s^{-1}), for electrons (dashed line) and for holes (dash-dotted line), and in case of $\mu_n = 1.0 \times 10^{3}$ m^2 V^{-1} s^{-1} ($\mu_p = 1.0 \times 10^{2}$ m^2 V^{-1} s^{-1}), for electrons (solid line) and for holes (dotted line).

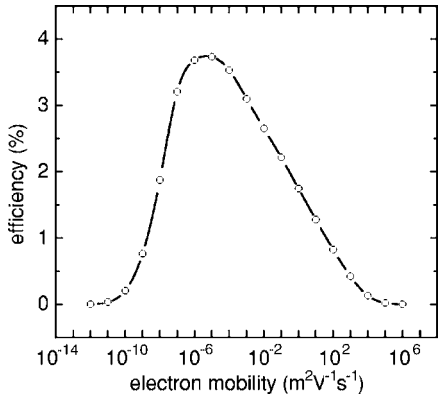

FIG. 5. Efficiency as a function of electron mobility, calculated for a P3HT:PCBM solar cell with an active layer of 100 nm, a maximum generation rate $G_{max} = 6.0 \times 10^{27}$ m^{-3} s^{-1}, a spatial average of the relative dielectric constant $\varepsilon_r = 3.4$, a semiconductor band gap $E_g = 1.0$ eV, and the dissociation parameters $a = 1.8$ nm and $k_F = 1.4 \times 10^4$ s^{-1}. A factor of 10 difference has been assumed between electron and hole mobility ($\mu_n : \mu_p = 10$).

crease. As a result, at low mobilites not only the increased recombination reduces the solar cell performance, but also the fact that many of the photogenerated bound electron-hole pairs will not dissociate into free carriers and recombine to their ground state. These results indicate that a high charge mobility is beneficial for the performance of an organic solar cell.

As a next step we evaluate the effect of an increasing carrier mobility, starting from a mobility of 1.0×10^{-5} m^2 V^{-1} s^{-1}. As can be seen in Fig. 3, the dissociation probability at maximum power point (M_{pp}) approaches 1 at this mobility and will not further increase, so the dissociation will not be further improved by a higher mobility value. However, as shown before, a low mobility leads to a buildup of charge carriers in the solar cell. Following the same reasoning one can expect that a high mobility, giving rise to an efficient extraction, will lead to a depletion of charge carriers in the solar cell. Thus, sweeping carriers efficiently out of the device will lead to low quasi-Fermi levels for electrons and holes.

Figure 4 shows that the V_{oc}, represented by the difference between the quasi-Fermi levels,[15] is reduced from 0.5 to 0.1 V when the mobility is increased from $\mu_n = 1.0 \times 10^{-5}$ m^2 V^{-1} s^{-1} to $\mu_n = 1.0 \times 10^{3}$ m^2 V^{-1} s^{-1}. This reduction of the V_{oc} leads to a decrease of the solar cell performance at very high carrier mobilities. As a final result in Fig. 5 the calculated efficiency is shown as a function of electron mobility, using the rest of the parameters equal to the ones found for the P3HT:PCBM solar cell.

It is observed that the efficiency exhibits a distinct maximum as a function of carrier mobility. Beyond the maximum efficiency located around $\mu_n = 1.0 \times 10^{-6} - 1.0 \times 10^{-5}$ m^2 V^{-1} s^{-1}, the efficiency decreases for both lower and higher mobilities. For lower mobilities the increased recombination and reduced dissociation probability decrease the efficiency, whereas the loss in V_{oc} at higher carrier mobility is responsible for the decrease of the efficiency. Furthermore, our calculations show that in the state-of-the-art BHJ solar cells of P3HT:PCBM, the experimentally measured carrier mobilities of $\sim 10^{-7}$ m^2 V^{-1} s^{-1} are already close to the maximum regarding the device efficiency values. As a result not much improvement is expected when the charge carrier transport properties are further enhanced. It should be noted that the optimum charge carrier mobility is, however, dependent on the light intensity. For light intensities larger than 1 sun the optimum will shift to higher mobilities, since the depletion of carriers at higher mobilities is reduced and the accumulation of carriers at low mobilities is increased.

In conclusion, we have shown that the maximum performance of organic BHJ solar cells is governed by the balance between transport and recombination of charge carriers. Both extremes of too low or too high mobility contribute to the losses in efficiency through different mechanisms. An optimized carrier mobility is therefore an important condition that must be fulfilled to obtain highly efficient organic solar cells.

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